

Appl. No. 09/238,851

Remarks/Arguments

Applicant wishes to thank the Examiner for his courtesy extended during the Examiner Interview of January 20, 2004.

Claims 1, 3, 5, 8, 10-12, 14-19 and 20-25 remain rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by U.S. Pat. No. 5,972,862 (the '862 Patent). Claim 18 remains rejected under 35 U.S.C. 103(a) as allegedly being obvious by the '862 patent and further in view of U. S. 6,117,783 (the '783 patent). Claims 1-17 remain rejected under 35 U.S.C. 103(a) as allegedly being obvious by the '862 patent and further in view of the '783 patent. Claims 1-13 and claims 18-26 are canceled herein. Claim 14 is amended herein to depend upon new claim 27 rather than canceled claim 1.

New claims 27-46 are added herein. It is submitted that new claims 27-46 raise no new issues and do not require the Examiner to conduct an additional search, since the claims merely clarify the subject matter already presented. For example, dependent claims 28-37, 40-42, and 44-45 contain similar subject matter to that previously presented in canceled claims 1-13 and 18-26.

As was discussed in our recent interview, new claims 27-46 include a recitation to the molar ratio. Independent claims 27 and 43 recite that the acidic buffer solution has, *inter alia*, "a molar ratio of acid to ammonium salt ranging from 10:1 to 1:10." Independent claim 38 recites that the acidic buffer solution has, *inter alia*, "a molar ratio of acetic acid to ammonium acetate ranging from 10:1 to 1:10". The aforementioned recitations are implicit and inherent within the definition of a buffer solution. The range of buffering effect of an acid and its conjugate base is approximately one pH unit on either side of the pK_a . See enclosure, Dean, J. A., Lange's Handbook of Chemistry 15th Ed., Mc-Graw Hill, Inc. (1999), § 8.3.3. Further, the molar ratio of acid to its conjugate base to provide such a buffering effect, i.e., a molar ratio ranging from 10:1 to 1:10, is well established in the art. See enclosure, Harris, D. C.,

Appl. No. 09/238,851

Quantitative Chemical Analysis, W. H. Freeman and Co., N.Y. (1999), pp. 222-224. See also, Mortimer, C. E., Chemistry: A Conceptual Approach, Litton Educational Publ. Co. (1971), pp. 562-564 (submitted in Applicant's Amendment and Response of January 16, 2003).

Dependent claims 39 and 46 recite that the molar ratio is substantially 1:1. Support for this claim recitation is provided, for example, in the specification at Example 1, page 7, lines 15-23.

As was discussed in our recent interview, the molar ratio recitation in new claims 27-46 is not anticipated nor rendered obvious by the art of record. In this connection, Applicant respectfully submits Exhibit 1. Exhibit 1 provides a table showing the formulations of Examples 1 through 5 and Comparative Examples 1 and 2 of the '862 patent and the formulation of Example 1 of the present application (see page 7, lines 15-23). Exhibit 1 further provides the molar ratios of acid to conjugate base of the various formulations. As Exhibit 1 illustrates, the only formulation in the '862 patent that has an acid and conjugate base pair is Example 4, which has acetic acid and trimethylammonium acetate (referred to in the '862 patent as TMBC). However, in the Example 4 formulation, the molar ratio of acetic acid to TMBC is .065, which falls outside of the effective buffering range, or the 10:1 to 1:10 range. Therefore, substantially no buffering effect is provided within this formulation. By contrast, Example 1 of the present application falls within the effective buffering range and has a substantially 1:1 molar ratio.

Appl. No. 09/238,851

SUMMARY

For at least the reasons set forth above, it is respectfully submitted that the above-identified application is in condition for allowance. Favorable reconsideration and prompt allowance of the claims are respectfully requested.

Should the Examiner believe that anything further is desirable in order to place the application in even better condition for allowance, the Examiner is invited to contact Applicants' undersigned Attorney at the telephone number listed below. Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

Respectfully submitted,



Rosaleen P. Morris-Oskanian
Registration No. 47,321
7201 Hamilton Boulevard
Allentown, PA 18195-1501
(610) 481-8169

encl.:

Petition for Three-Month Extension of Time
Exhibit 1
References (2)
Fee Calculation Sheet

**EXHIBIT 1: Comparison of Formulations of U.S. Patent No. 5,972,862 to
Exemplary Formulation in USSN 09/238,581**

Formulation	Ammmonium Fluoride (wt%)	Organic Carboxylic Acid (wt%)	Organic Solvent (wt%)	Salt (wt%)	Surfactant (wt%)	Molar Ratio Acid/Conjugate Base ⁽¹⁾	Comments
Ex. 1 of '862	8	Propionic (1)	DMF (40)	TMAF (5)	EP-120A (.1)	No Buffer	
Ex. 2 of '862	8	Phthalic Anhydride (.1)	Formamide (40)	TMAF (5)	EP-120A (.1)	No Buffer	
Ex. 3 of '862	5	Isobutyric (.2)	DMAC (35)	TMAF (10)	EP-120A (.1)	No Buffer	
Ex. 4 of '862	10	Acetic (.1)	DMF (45)	TMBC (3)	EP-120A (.1)	.065	Outside of effective buffering range
Ex. 5 of '862	1	Boric (.3)	DMF (69)	--	--	No Buffer	
Reference Ex. of '862	8	Propionic (2)	DMF (40)	TMAF (5)	--	No Buffer	
Comparative Ex. 1 of '862	8	--	DMF (40)	TMAF (5)	EP-120A (.1)	No Buffer	
Comparative Ex. 2 of '862	1	--	DMF (69)	--	--	No Buffer	
Ex. 1 of 09/238,851	2.6 (40% aqueous)	Acetic (12)	DMAC (57.5)	Ammonium Acetate (15.2)	--	~1	Within effective buffering range

⁽¹⁾ For an effective buffer, the molar concentration ratio of the acid to its conjugate base should range from 10/1 to 1/10, or 0.1 to 10. This concentration range is equivalent to a + or - 1 pH unit on each side of the pK_a . See Harris, D. C., Quantitative Chemical Analysis, W. H. Freeman and Co., N.Y. (1999), pp. 222-224 and Mortimer, C. E., Chemistry: A Conceptual Approach, Littton Educational Publ. Co. (1971), pp. 562-564.

Quantitative Chemical Analysis

FIFTH EDITION

Daniel C. Harris

Michelson Laboratory
China Lake, California



W. H. Freeman and Company
New York

Acquisitions Editor: Michelle Russell Juliet
Marketing Manager: Kimberly Manzi
Project Editor: Mary Louise Byrd
Cover Designer: Blake Logan
Text Designer: Diana Blume
Illustration Coordinator: Susan Wein
Illustrator: Network Graphics
Production Coordinator: Paul W. Rohloff
Associate Media and Supplements Editor: Matthew P. Fitzpatrick
Composition: Black Dot Graphics
Manufacturing: RR Donnelley & Sons Company

COVER IMAGE: Montserrat, Soufrière Hills volcano. August 19, 1997.
CREDIT: AP/Wide World Photos/Kevin West

Library of Congress Cataloging-in-Publication Data

Harris, Daniel C., 1948—
Quantitative chemical analysis/Daniel C. Harris.—5th ed.
p. cm.
Includes index.
ISBN 0-7167-2881-8
1. Chemistry, Analytic—Quantitative. I. Title.
QD101.2.H37 1998
545—dc21

97-48837
CIP

© 1982, 1987, 1991, 1995, 1999 by W. H. Freeman and Company

No part of this book may be reproduced by any mechanical, photographic, or electronic process, or in the form of a phonographic recording, nor may it be stored in a retrieval system, transmitted, or otherwise copied for public or private use, without written permission from the publisher.

Printed in the United States of America

First printing 1998

F-194 900/3006 089-1

JAN-19-2004 12:03PM FRSB

4222
10 Monoprotic Acid-Base Equilibria

Isomer of hydroxybenzoic acid	K_a	K_b
Ortho	1.07×10^{-3}	9.35×10^{-12}
Para	2.63×10^{-5}	3.80×10^{-10}

Using each value of K_b , and letting $F = 0.0500 \text{ M}$, we find

$$\text{pH of } 0.0500 \text{ M } o\text{-hydroxybenzoate} = 7.83$$

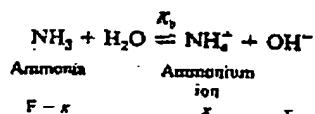
$$\text{pH of } 0.0500 \text{ M } p\text{-hydroxybenzoate} = 8.64$$

These are reasonable pH values for solutions of weak bases. Furthermore, as expected, the conjugate base of the stronger acid is the weaker base.

EXAMPLE A Volumetric Reaction Problem

Find the pH of 0.10 M ammonia.

SOLUTION When ammonia is dissolved in water, its reaction is



In Appendix G we find ammonium ion, NH_4^+ , listed next to ammonia. pK_a for ammonium ion is 9.244. Therefore, K_b for NH_3 is

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14.00}}{10^{-9.244}} = 1.75 \times 10^{-5}$$

To find the pH of 0.10 M NH_3 , we set up and solve the equation

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.10 - x} = K_b = 1.75 \times 10^{-5}$$

$$x = [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = 7.6 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = 11.12$$

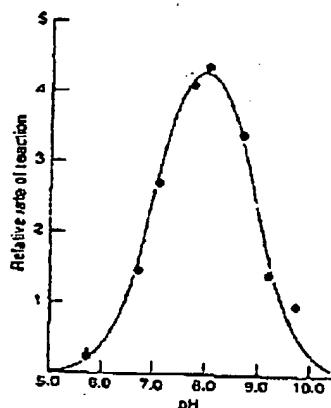
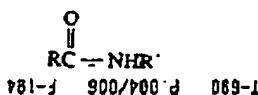


Figure 10-3 pH dependence of the rate of cleavage of an amide bond by the enzyme chymotrypsin. The rate near pH 8 is twice as great as the rate near pH 7 or pH 9. Chymotrypsin helps digest proteins in your intestine. (M. L. Bender, G. E. Clement, F. J. Kozdy, and H. A. Heck, *J. Am. Chem. Soc.* 1964, 86, 3680.)



10-5 Buffers

A buffered solution resists changes in pH when acids or bases are added or when dilution occurs. The buffer is a mixture of an acid and its conjugate base. There must be comparable amounts of the conjugate acid and base (say, within a factor of 10) to exert significant buffering.

The importance of buffers in all areas of science is immense. Biochemists are particularly concerned with buffers because the proper functioning of any biological system depends on pH. For example, Figure 10-3 shows how the rate of one particular enzyme-catalyzed reaction varies with pH. For an organism to survive,

Mixing a Weak Acid and Its Conjugate Base

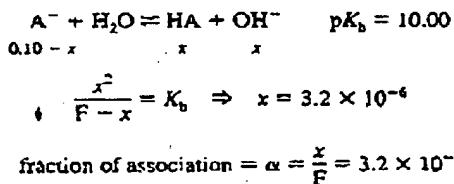
If you mix A moles of a weak acid with B moles of its conjugate base, the moles of acid remain close to A and the moles of base remain close to B . Very little reaction occurs to change either concentration.

To understand why this should be so, look at the K_a and K_b reactions in terms of Le Châtelier's principle. Consider an acid with $pK_a = 4.00$ and its conjugate base with $pK_b = 10.00$. Let's calculate the fraction of acid that dissociates in a 0.10 M solution of HA:

$$\begin{array}{rcl} \text{HA} & \rightleftharpoons & \text{H}^+ + \text{A}^- \\ 0.10 - x & & x \\ \frac{x^2}{F-x} = K_a & \Rightarrow & x = 3.1 \times 10^{-2} \\ \text{fraction of dissociation} = \alpha = \frac{x}{F} & = & 0.031 \end{array}$$

The acid is only 3.1% dissociated under these conditions.

In a solution containing 0.10 mol of A^- dissolved in 1.00 L, the extent of reaction of A^- with water is even smaller:



HA dissociates very little, and adding extra A^- to the solution will make the HA dissociate even less. Similarly, A^- does not react very much with water, and adding extra HA makes A^- react even less. If 0.050 mol of A^- plus 0.036 mol of HA are added to water, there will be close to 0.050 mol of A^- and close to 0.036 mol of HA in the solution at equilibrium.

Henderson-Hasselbalch Equation

The central equation for buffers is the Henderson-Hasselbalch equation, which is merely a rearranged form of the K_a equilibrium expression.

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \\ \log K_a &= \log \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \log [\text{H}^+] + \log \frac{[\text{A}^-]}{[\text{HA}]} \\ -\log [\text{H}^+] &= -\log K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \\ \text{pH} &\quad \text{p}K_a \end{aligned}$$

Henderson-Hasselbalch equation: $\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$ (10-16)

223

10-5 Buffers

When you mix a weak acid with its conjugate base, you get what you mix!

The approximation that the concentrations of HA and A^- remain unchanged breaks down for dilute solutions or at extremes of pH. We will test the validity of the approximation at the end of this chapter.

$$\log xy = \log x + \log y$$

The names of Henderson and Hasselbalch appear to be associated with Equation 10-16 because they recognized that the concentrations $[\text{A}^-]$ and $[\text{HA}]$ can be set equal to their formal concentrations, and they were among the first people to apply the equation to practical problems.

224

10 Monoprotic Acid-Base Equilibria

Equations 10-16 and 10-17 are only sensible when the base (A^- or B) is in the numerator. When the concentration of base increases, the log term increases and the pH increases.

The Henderson-Hasselbalch equation tells us the pH of a solution, provided we know the ratio of the concentrations of conjugate acid and base, as well as pK_a for the acid. If a solution is prepared from the weak base B and its conjugate acid, the analogous equation is

$$pH = pK_a + \log \frac{[B]}{[BH^+]} \quad pK_a \text{ applies to this acid} \quad (10-17)$$

where pK_a is the acid dissociation constant of the weak acid BH^+ . The important features of Equations 10-16 and 10-17 are that the base (A^- or B) appears in the numerator of both equations, and the equilibrium constant is K_a of the acid in the denominator.

Challenge Show that when activities are not neglected, the correct form of the Henderson-Hasselbalch equation is

$$pH = pK_a + \log \frac{[A^-] \gamma_{A^-}}{[HA] \gamma_{HA}} \quad (10-18)$$

Properties of the Henderson-Hasselbalch Equation

When $[A^-] = [HA]$, $pH = pK_a$.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = pK_a + \log 1 = pK_a$$

Table 10-1
Effect of $[A^-]/[HA]$ on pH

$[A^-]/[HA]$	pH
100:1	$pK_a + 2$
10:1	$pK_a + 1$
1:1	pK_a
1:10	$pK_a - 1$
1:100	$pK_a - 2$

Regardless of how complex a solution may be, whenever $pH = pK_a$, $[A^-]$ must equal $[HA]$. This relation is true because all equilibria must be satisfied simultaneously in any solution at equilibrium. If there are 10 different acids and bases in the solution, the 10 forms of Equation 10-16 must all give the same pH, because there can be only one concentration of H^+ in a solution.

Another feature of the Henderson-Hasselbalch equation is that for every power-of-10 change in the ratio $[A^-]/[HA]$, the pH changes by one unit (Table 10-1). As the base (A^-) increases, the pH goes up. As the acid (HA) increases, the pH goes down. For any conjugate acid-base pair, you can say, for example, that if $pH = pK_a - 1$, there must be 10 times as much HA as A^- . Therefore ten-elevenths is in the form HA and one-eleventh is in the form A^- .

EXAMPLE Using the Henderson-Hasselbalch Equation

Sodium hypochlorite ($NaOCl$, the active ingredient of almost all bleaches) was dissolved in a solution buffered to pH 6.20. Find the ratio $[OCl^-]/[HOCl]$ in this solution.

SOLUTION In Appendix G we find that $pK_a = 7.53$ for hypochlorous acid, HOCl. The pH is known, so the ratio $[OCl^-]/[HOCl]$ can be calculated from the Henderson-Hasselbalch equation.



$$pH = pK_a + \log \frac{[OCl^-]}{[HOCl]}$$

Jan-18-2004 12:04pm From: 900/006 089-1

LANGE'S HANDBOOK OF CHEMISTRY

John A. Dean
Professor Emeritus of Chemistry
University of Tennessee, Knoxville

Fifteenth Edition

McGRAW-HILL, INC.
New York St. Louis San Francisco Auckland Bogotá
Caracas Lisbon London Madrid Mexico Milan
Montreal New Delhi Paris San Juan São Paulo
Singapore Sydney Tokyo Toronto

Copyright © 1999, 1992, 1985, 1979, 1973, 1967, 1961, 1956 by McGraw-Hill, Inc. All rights reserved.

Copyright renewed 1972 by Norbert Adolph Lange.

Copyright 1952, 1949, 1946, 1944, 1941, 1939, 1937, 1934 by McGraw-Hill, Inc. All rights reserved. Printed in the United States of America. Except as permitted under the United States Copyright Act of 1976, no part of this publication may be reproduced or distributed in any form or by any means, or stored in a data base retrieval system without the prior written permission of the publisher.

5 6 7 8 9 0 DOC/DOC 9 0 3 2 1 0 9 8

ISBN 0-07-016384-7

The sponsoring editor for this book was Robert Esposito, and the production supervisor was Clare B. Stanley. It was set in Times Roman by Progressive Information Technologies.

Printed and bound by R. R. Donnelley & Sons Company.

Information contained in this work has been obtained by McGraw-Hill, Inc., from sources believed to be reliable. However, neither McGraw-Hill nor its authors guarantee the accuracy or completeness of any information published herein and neither McGraw-Hill nor its authors shall be responsible for any errors, omissions, or damages arising out of use of this information. This work is published with the understanding that McGraw-Hill and its authors are supplying information but are not attempting to render engineering or other professional services. If such services are required, the assistance of an appropriate profession should be sought.

8.110

SECTION 8

8.3.3 Buffer Solutions Other Than Standards

The range of the buffering effect of a single weak acid group is approximately one pH unit on either side of the pK_a . The ranges of some useful buffer systems are collected in Table 8.19. After all the components have been brought together, the pH of the resulting solution should be determined at the temperature to be employed with reference to standard reference solutions. Buffer components should be compatible with other components in the system under study; this is particularly significant for buffers employed in biological studies. Check tables of formation constants to ascertain whether metal-binding character exists.

TABLE 8.19 pH Values of Biological and Other Buffers for Control Purposes

Materials	Acronym	pK_a	pH range
<i>p</i> -Toluenesulfonate and <i>p</i> -toluenesulfonic acid		1.7	1.1-3.3
Glycine and HCl		2.35	1.0-3.7
Citrate and HCl		3.13	1.3-4.7
Formate and HCl		3.71	2.8-4.6
Succinate and borax		4.21, 5.64	3.0-5.8
Phenyl acetate and HCl		4.31	3.5-5.0
Acetate and acetic acid		4.76	3.7-5.6
Succinate and succinic acid		4.21, 5.64	4.8-6.3
2-(<i>N</i> -Morpholino)ethanesulfonic acid	MES	6.1	5.5-6.7
Bis(2-hydroxyethyl)iminotriis(hydroxymethyl)methane	BIS-TRIS	6.5	5.8-7.2
KH_2PO_4 and borax		2.2, 7.2; 9	5.8-9.2
<i>N</i> -(2-Acetamido)-2-aminodiacetic acid	ADA	6.6	6.0-7.2
2-(2-Amino-2-oxethyl)aminoethanesulfonic acid	ACES	6.8	6.1-7.5
Piperazine- <i>N,N'</i> -bis(2-ethanesulfonic acid)	PIPES	6.8	6.1-7.5
3-(<i>N</i> -Morpholino)-2-hydroxypropanesulfonic acid	MOPS	6.9	6.2-7.6
1,3-Bis[tris(hydroxymethyl)methyl]amino propane	BIS-TRIS PROPANE	6.9, 9.0	6.3-9.5
KH_2PO_4 and Na_2HPO_4		7.2	6.1-7.5
<i>N,N</i> -Bis(2-hydroxyethyl)-2-aminoethanesulfonic acid	BES	7.1	6.4-7.8
3-(<i>N</i> -Morpholino)propansulfonic acid	MOPS	7.2	6.5-7.9
<i>N</i> -(2-Hydroxyethyl)piperazine- <i>N'</i> -(2-ethanesulfonic acid)	HEPES	7.5	6.8-8.2
<i>N</i> -Tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid	TES	7.5	6.8-8.2
3-[<i>N,N</i> -Bis(2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid	DIPSO	7.6	7.0-8.2
3-[<i>N</i> -(<i>N</i> -tris(hydroxymethyl)methyl)amino]-2-hydroxypropanesulfonic acid	TAPSO	7.6	7.0-8.2
5,5-Diethylbarbiturate (veronal) and HCl		8.0	7.0-8.5
Tris(hydroxymethyl)aminocarbonyl	TRIZMA	8.1	7.0-9.1
<i>N</i> -(2-hydroxyethyl)piperazine- <i>N'</i> -(2-hydroxypropanesulfonic acid)	HEPPSO	7.8	7.1-8.3
Piperazine- <i>N,N'</i> -bis(2-hydroxypropanesulfonic acid)	POPSO	7.8	7.2-8.5
Triethanolamine	TEA	7.8	6.9-8.5
<i>N</i> -Tris(hydroxymethyl)methylglycine	TRICINE	8.1	7.4-8.8
Borax and HCl			7.6-8.9
<i>N,N</i> -Bis(2-hydroxyethyl)glycine	BICINE	8.3	7.6-9.0
<i>N</i> -Tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid	TAPS	8.4	7.7-9.1
3-(1,1-Dimethyl-2-hydroxyethyl)-2-hydroxypropanesulfonic acid	AMPSO	9.0	8.3-9.7
Ammonia (aqueous) and NH ₄ Cl		9.2	8.3-9.2
2-(<i>N</i> -Cyclohexylamino)-2-hydroxy-1-propanesulfonic acid	CHES	9.3	8.6-10.0

ELECTROLYTES, SMF, AND CHEMICAL EQUILIBRIUM

8.111

TABLE 8.19 pH Values of Biological and Other Buffers for Control Purposes (Continued)

Materials	Acronym	pK _a	pH range					
Glycine and NaOH		9.7	8.2–10.1					
Ethanolamine (2-aminoethanol) and HCl		9.5	8.6–10.4					
3-(Cyclohexylamino)-2-hydroxy-1-propanesulfonic acid	CAPS0	9.6	8.9–10.3					
2-Amino-2-methyl-1-propanol	AMP	9.7	9.0–10.5					
Carbonate and hydrogen carbonate		10.3	9.2–11.0					
Borax and NaOH			9.4–11.1					
3-(Cyclohexylamino)-1-propanesulfonic acid	CAPS	10.4	9.7–11.1					
Na ₂ HPO ₄ and NaOH		11.9	11.0–12.0					
<i>x</i> mL of 0.2 <i>M</i> Sodium Acetate (27.199 g NaOAc · 3H ₂ O per liter) plus <i>y</i> mL of 0.2 <i>M</i> Acetic Acid		<i>x</i> mL of 0.1 <i>M</i> KH ₂ PO ₄ (13.617 g · L ⁻¹) plus <i>y</i> mL of 0.05 <i>M</i> Borax Solution (19.404 g Na ₂ B ₄ O ₇ · 10H ₂ O per liter)						
pH	NaOAc, mL	Acetic Acid, mL	pH	KH ₂ PO ₄ , mL	Borax, mL	pH	KH ₂ PO ₄ , mL	Borax, mL
3.60	7.5	92.5	5.80	92.1	7.9	7.60	51.7	48.3
3.80	12.0	88.0	6.00	87.7	12.0	7.80	49.2	50.8
4.00	18.0	82.0	6.200	83.0	17.0	8.00	46.5	53.5
4.20	26.5	73.5	6.40	77.8	22.2	8.20	43.0	57.0
4.40	37.0	63.0	6.60	72.2	27.8	8.40	38.7	61.3
4.60	49.0	51.0	6.80	66.7	33.3	8.60	34.0	66.0
4.80	60.0	40.0	7.00	62.3	37.7	8.80	27.6	72.4
5.00	70.5	29.5	7.20	58.8	41.9	9.00	17.5	82.5
5.20	79.0	21.0	7.40	55.0	45.0	9.20	5.0	95.0
5.40	85.5	14.5						
5.60	90.5	9.5						
<i>x</i> mL of Veronal (20.6 g Na Diethylbarbiturate per liter) plus <i>y</i> mL of 0.1 <i>M</i> HCl		<i>x</i> mL of 0.2 <i>M</i> Aqueous NH ₃ Solution plus <i>y</i> mL of 0.2 <i>M</i> NH ₄ Cl (10.699 g · L ⁻¹)		<i>x</i> mL of 0.1 <i>M</i> Citrate (21.0 g Citric Acid Monohydrate + 200 mL 1 <i>M</i> NaOH per liter) plus <i>y</i> mL of 0.1 <i>M</i> NaOH				
pH	Veronal, mL	HCl, mL	pH	Aq NH ₃ , mL	NH ₄ Cl, mL	pH	Citrate, mL	NaOH, mL
7.00	53.6	46.4	8.00	5.5	94.5	5.10	90.0	10.0
7.20	55.4	44.6	8.20	8.5	91.5	5.30	80.0	20.0
7.40	58.1	41.9	8.40	12.5	87.5	5.50	71.0	29.0
7.60	61.5	38.5	8.60	18.5	81.5	5.70	67.0	33.0
7.80	66.2	33.8	8.80	26.0	74.0	5.90	62.0	38.0
8.00	71.6	28.4	9.00	36.0	64.0			
8.20	76.9	23.1	9.25	50.0	50.0			
8.40	82.3	17.7	9.40	58.5	41.5			
8.60	87.1	12.9	9.60	69.0	31.0			
8.80	90.8	9.2	9.80	78.0	22.0			
9.00	93.6	6.4	10.00	85.0	15.0			

ELECTROLYTES, EMP, AND CHEMICAL EQUILIBRIUM

8.113

When there are two or more acid groups per molecule, or a mixture is composed of several overlapping acids, the useful range is larger. Universal buffer solutions consist of a mixture of acid groups which overlap such that successive K_a values differ by 2 pH units or less. The Pridaux-Ward mixture comprises phosphate, phenyl acetate, and borate plus HCl and covers the range from 2 to 12 pH units. The McIlvaine buffer is a mixture of citric acid and Na_2HPO_4 that covers the range from pH 2.2 to 8.0. The Britton-Robinson system consists of acetic acid, phosphoric acid, and boric acid plus NaOH and covers the range from pH 4.0 to 11.5. A mixture composed of Na_2CO_3 , NaH_2PO_4 , citric acid, and 2-amino-2-methyl-1,3-propanediol covers the range from pH 2.2 to 11.0.

General directions for the preparation of buffer solutions of varying pH but fixed ionic strength are given by Bates.^a Preparation of McIlvaine buffered solutions at ionic strengths of 0.5 and 1.0 and Britton-Robinson solutions of constant ionic strength have been described by Elving et al.^b and Frugoni,^c respectively.

^a Bates, *Determination of pH, Theory and Practice*, Wiley, New York, 1964, pp. 121-122.^b Shrag, Markowitz, and Rosenblat, *Anal. Chem.*, 28:1179 (1956).^c Frugoni, *Gazz. Chim. Ital.*, 87:L403 (1957).

8.4 REFERENCE ELECTRODES

TABLE 8.20 Potentials of Reference Electrodes in Volts as a Function of Temperature
Liquid-junction potential included.

Temp., °C	0.1M KCl Calomel ^a	1.0M KCl Calomel ^a	3.5M KCl Calomel ^a	Satd. KCl Calomel ^a	1.0M KCl Ag/AgCl ^b	1.0M KBr Ag/AgCl ^b	1.0M KI Ag/AgCl ^b
0	0.3367	0.2883		0.25918	0.23655	0.08128	-0.14637
5					0.23413	0.07961	-0.14719
10	0.3362	0.2868	0.2556	0.25387	0.23142	0.07773	-0.14822
15	0.3361			0.2511	0.22857	0.07572	-0.14942
20	0.3358	0.2844	0.2520	0.24775	0.22557	0.07349	-0.15081
25	0.3356	0.2830	0.2501	0.24453	0.22234	0.07106	-0.15244
30	0.3354	0.2815	0.2481	0.24118	0.21904	0.06856	-0.15405
35	0.3351			0.2376	0.21565	0.06585	-0.15590
38	0.3350		0.2448	0.2355			
40	0.3345	0.2782	0.2439	0.23449	0.21208	0.06310	-0.15788
45					0.20835	0.06012	-0.15998
50	0.3315	0.2745		0.22737	0.20449	0.05704	-0.16219
55					0.20056		
60	0.3248	0.2702		0.2235	0.19649		
70					0.18782		
80				0.2083	0.1787		
90					0.1693	0.0251	

^a Bates et al., *J. Research Natl. Bur. Standards*, 45, 418 (1950).^b Bates and Bower, *J. Research Natl. Bur. Standards*, 53, 283 (1954).^c Hezlet, Robinson and Bates, *J. Phys. Chem.*, 66, 1423 (1962).^d Hezlet, Robinson and Bates, *J. Phys. Chem.*, 68, 1929 (1964).

*** TOTAL PAGE.10 **